

GEOCHEMICAL CHARACTERIZATION OF SOIL ORGANIC MATTER AND VARIABILITY OF A POSTGLACIAL DETRITAL ORGANIC SUPPLY (CHAILLEXON LAKE, FRANCE)

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ABSTRACT

Geochemical analysis of sedimentary organic matter in recent lacustrine sediments appears to be a useful tool in providing information concerning past environmental conditions. However, such analysis is often made without knowing the geochemical characteristics of the organic matter derived from the watershed and, more explicitly, its soils. The present work deals with (i) a geochemical investigation (Rock-Eval pyrolysis) of soil organic matter sampled in a lake watershed, and (ii) the study of the sedimentary organic matter trapped in the lake deposits. The research was conducted on Chaillexon Lake which was created by a rock collapse that dammed the palaeovalley of the Doubs River about 12 000 years ago. Since this event, the sediment trap provides a continuous palaeoclimatic record for the Postglacial period.

Results obtained lead to two main conclusions. First, the variability of Rock-Eval pyrolysis values observed in soils modifies the common interpretation given to these parameters in the characterization of sedimentary organic matter. Indeed, variations in these parameters point not only to varying proportions of terrestrial and lacustrine organic matter in a lacustrine infilling but also to variations of the terrestrial supply linked with the evolution of vegetal cover in the catchment. The second conclusion is that the story of the Chaillexon lacustrine system is marked by a rather sudden soil and forest development at the Preboreal–Boreal transition (9000 BP). © 1998 John Wiley & Sons, Ltd.

KEY WORDS: humus layers; organic sedimentation; palaeoclimates; Postglacial period; organic geochemistry; Rock-Eval pyrolysis

INTRODUCTION

Study of organic matter (OM) in sediments has recently become the subject of a considerable amount of work through both geochemical and petrological approaches (Connan, 1987; Huc, 1988). Such interest in OM is motivated by its lability which makes it an excellent recorder of past environmental conditions and past changes. Following the description of OM in many marine basins (e.g. Crumière *et al.*, 1990; Herbin *et al.*, 1987), continental series, in spite of their scarcity (Reille and De Beaulieu, 1988) are also becoming attractive for palaeoclimatologists. High primary biological productivity (on the watershed and/or in the water column), high sedimentation rates and efficient preservation conditions make lake sedimentary infillings very good sinks and recorders of OM (Huc, 1988; Kelts, 1988; De Deckker, 1988). Moreover, in an attempt to promote high temporal resolution, it appears necessary to favour Quaternary sequences.

Up to now, few studies have attempted to define the relationships between changes in OM characteristics and climatic 'forcing'. Bertrand *et al.* (1992), Brocero (1991), Lallier-Verges *et al.* (1993), Sifeddine *et al.* (1994) and Sifeddine (1991) recently presented studies on temperate and tropical lakes (Le Bouchet, Haute Loire, France & Carajas, Amazonie, Brazil) presenting sequences from the Late Quaternary period (350–600 000 years BP). However, such analyses are often made without knowing the characteristics of the OM produced in the watershed and, particularly, in the soils. Rock-Eval pyrolysis – a petroleum exploration technique (Espitalié *et al.*, 1985a) – gives general information about the origin of the sedimentary OM that can

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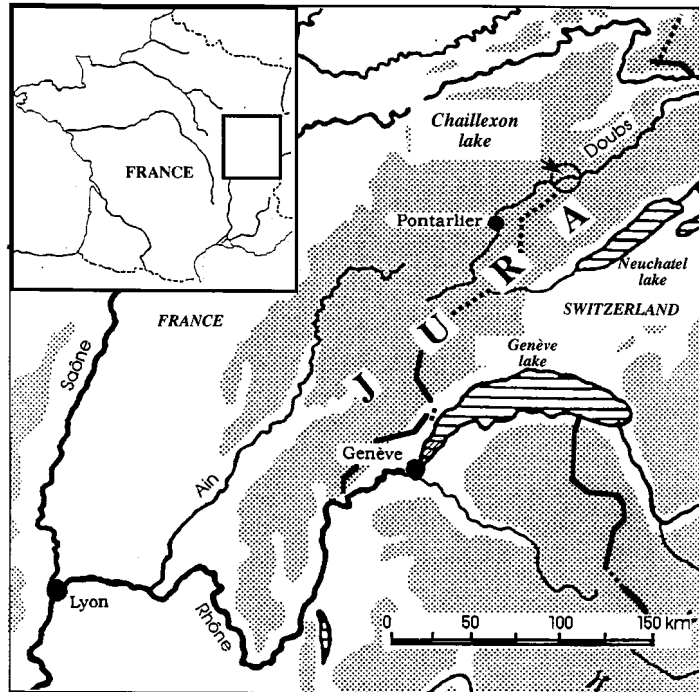


Figure 1. Location of the study area

be lacustrine or terrestrial (Scribe and Bourdier, 1995). However, users tend not to take into account the fact that this technique is suitable only for samples which have previously undergone a thermal diagenetic history. Consequently, its application to recent sediment shows some limitations related to its working principal. One limitation is the variability of terrestrial OM.

The present work deals with: (i) the characterization of geochemical organic markers (Rock-Eval pyrolysis technique) in different soil humus layers in a lake watershed; (ii) the occurrence of these markers in the corresponding lake sediments; and (iii) the story of the lacustrine system

The study was made on a hard water lake in a temperate climate: Chailloux Lake (Jura, France). The sedimentary basin is characterized by a high sedimentation rate (up to 10 mm a^{-1}) which is favourable to OM preservation. In addition, climatic changes in the region during the Late Glacial period are well documented (Richard, 1988).

STUDY AREA AND SAMPLING

Chailloux Lake and its watershed

Chailloux Lake is located in the Upper Valley of the Doubs River at the border between France and Switzerland (Figure 1). The lake formed after a rock collapse which dammed the Doubs River 12 000 years ago, after the retreat of the Würmian glacier (Schardt, 1909). Today, 90 per cent of the original available capacity is filled by sediment brought down by the Doubs River (Campy *et al.*, 1985, 1994a; Campy and Macaire, 1989). The watershed (910 km^2) (Campy *et al.*, 1994b) consists of a Meso-Cenozoic substratum composed of marls and limestones at an altitude which varies from 1460 to 752 m.

Humus layers in the watershed

Investigations were limited to the upper soil layers (0–20 cm depth) because of their high tendency to be eroded. Soil sampling was conducted by considering that vegetation plays a major role in controlling soil formation and evolution, soil development being also dependent on hydrological conditions (Duchaufour,

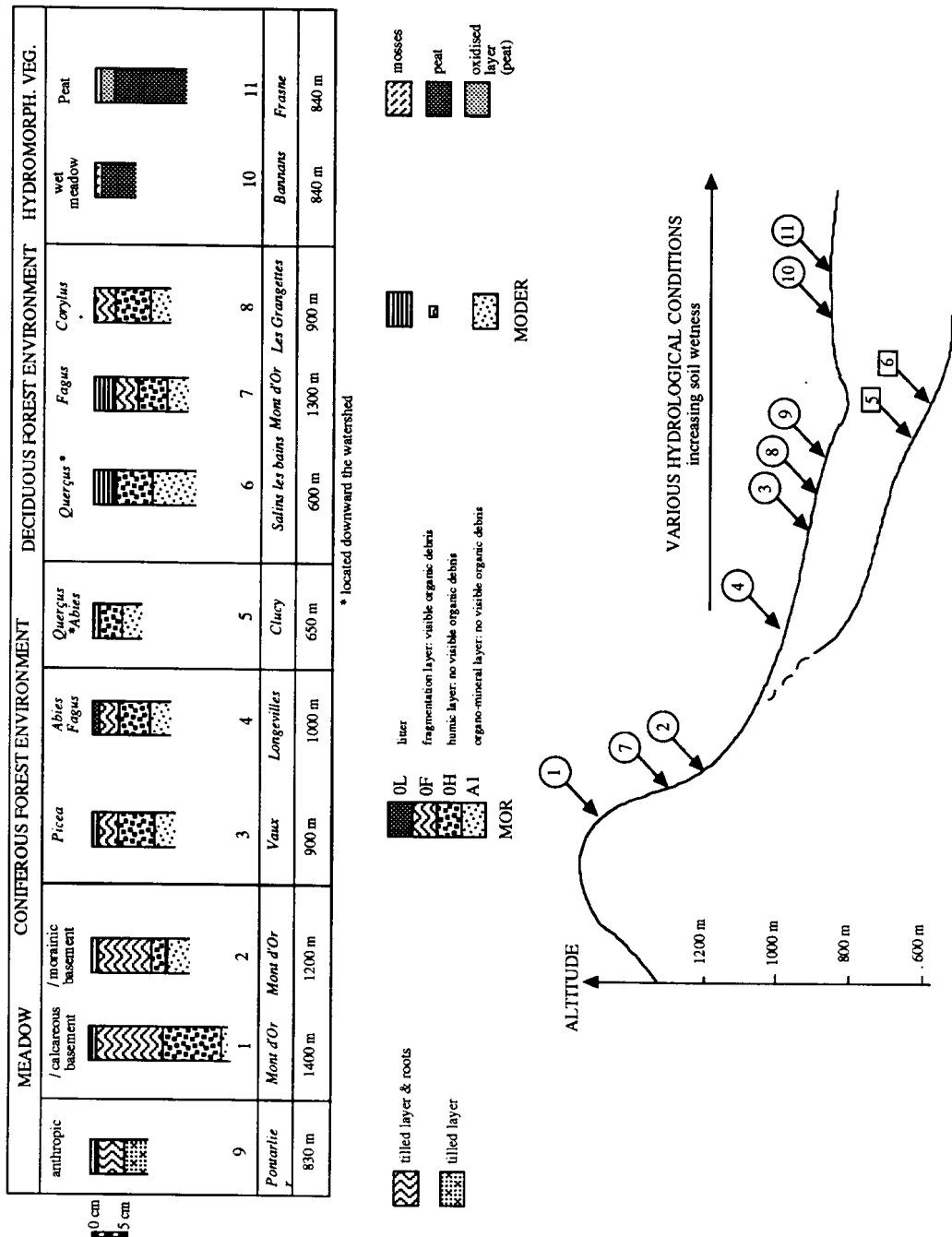


Figure 2. Sampling location and description of the soil humus layers

1977). Eleven humus layers were analysed. They are distributed downward along the watershed (Figure 2): (i) an altitudinal transect from deciduous trees, then to conifers and meadows; and (ii) a transverse transect guided by variations of hydrological conditions from dry to wet environments.

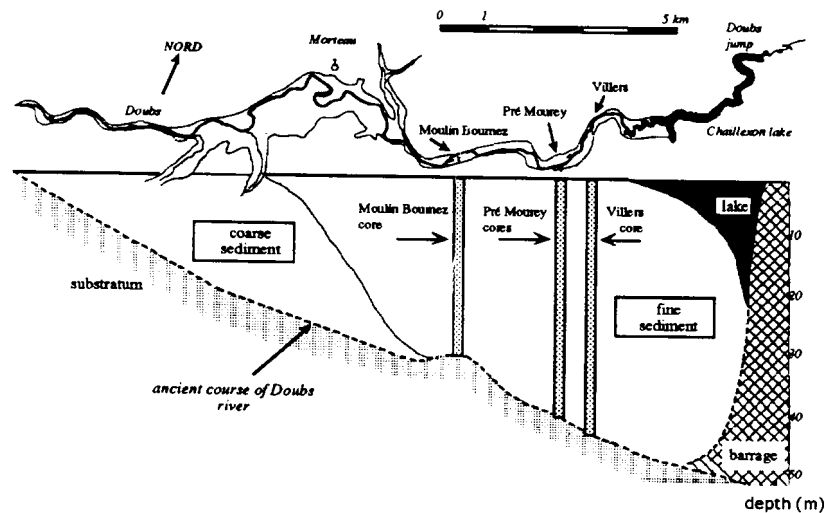


Figure 3. The post-glacial lacustrine infilling of Chailloux Lake

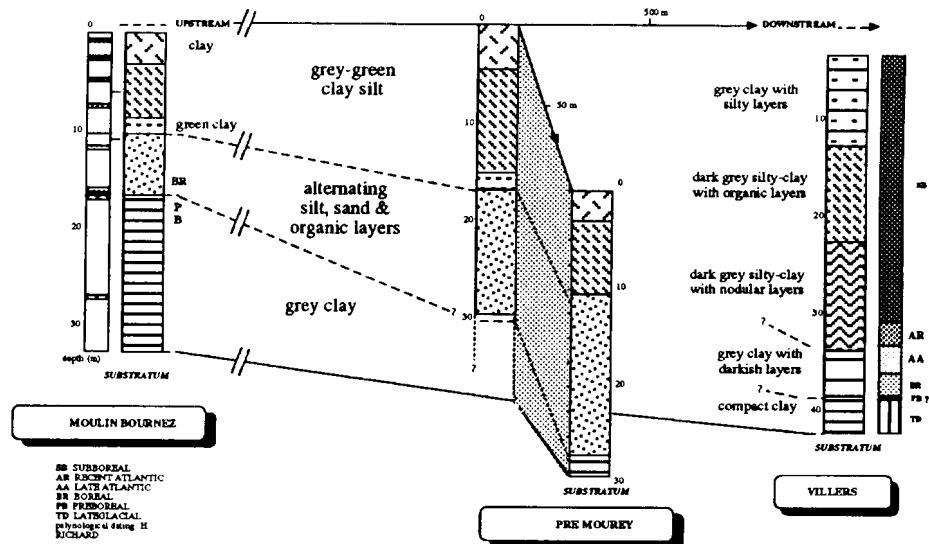


Figure 4. Gross stratigraphy and lithology of the Chailloux basin

Following the nomenclature of Jabiol *et al.* (1994), the humus layers were divided into three sublayers: OL at the top, which is the litter made of weakly fragmented twigs and leaves; OF, composed of leaf fragments and organic faecal pellets resulting from the decomposition activity of the soil mesofauna; and OH, the basal layer, made up exclusively of faecal pellets. Just beneath lies the A1 horizon where OM is associated with the mineral fraction.

Lake sediments

Campy *et al.* (1994b) distinguished two major accumulations in the sedimentary fill (Figure 3). These are a coarse detrital accumulation dated from the Alleröd period in the upstream system and a fine muddy accumulation dated from Alleröd to Present in the downstream part. The chronology is based on palynological data and 17 radiocarbon dates (Campy *et al.*, 1994b).

From upstream to downstream, fine sediment has settled in prograding systems which reach a maximal thickness of 50 m. The present study is based on three cores (Moulin Bourneux, Pré Mourey, Villers le lac;

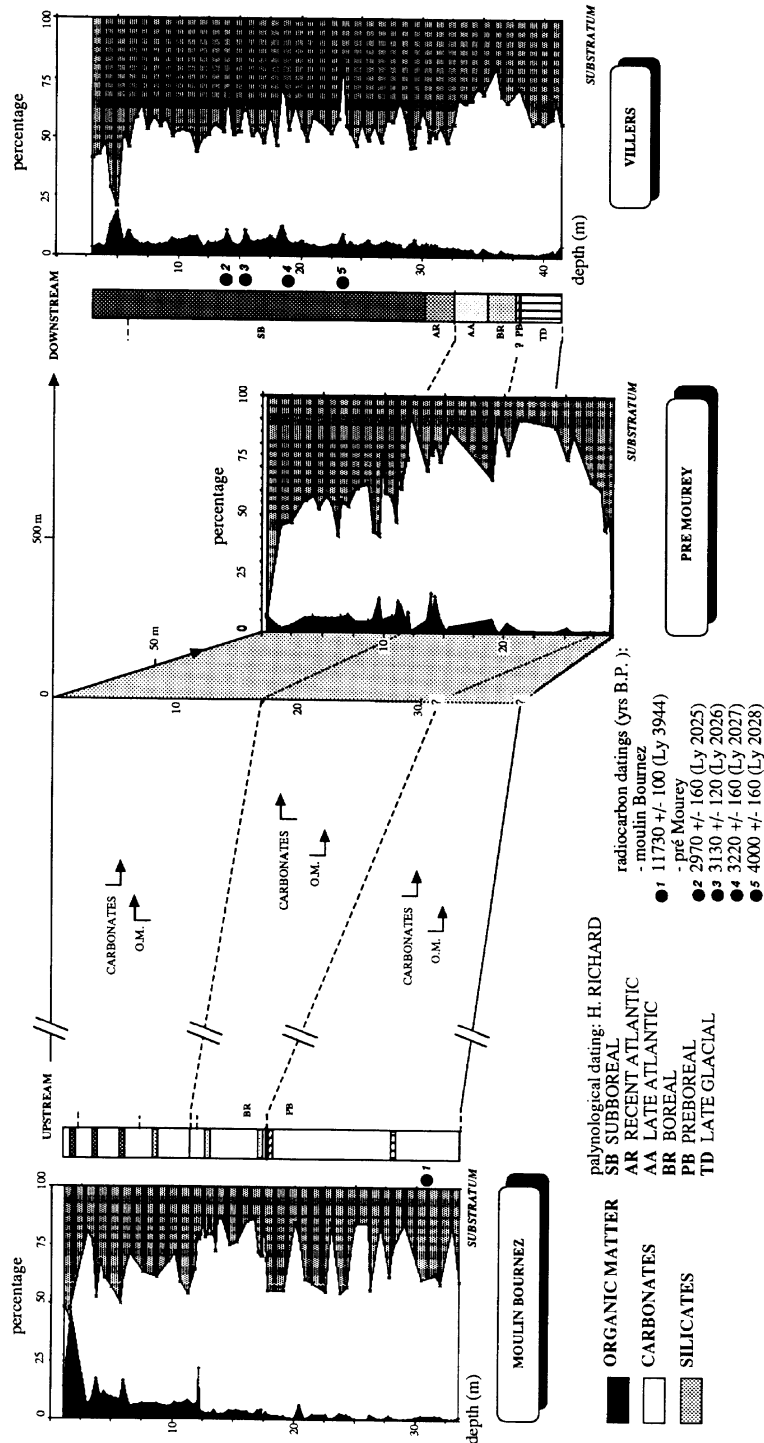


Figure 5. Composition of the sediment core correlation

Figure 3) which penetrated the fine sedimentary unit. These three cores successively penetrated three main lithological units allowing core-to-core correlations (Di-Giovanni *et al.*, 1992; Di-Giovanni, 1994; Campy *et al.*, 1994b). From bottom to top, one successively observes (Figures 4 and 5):

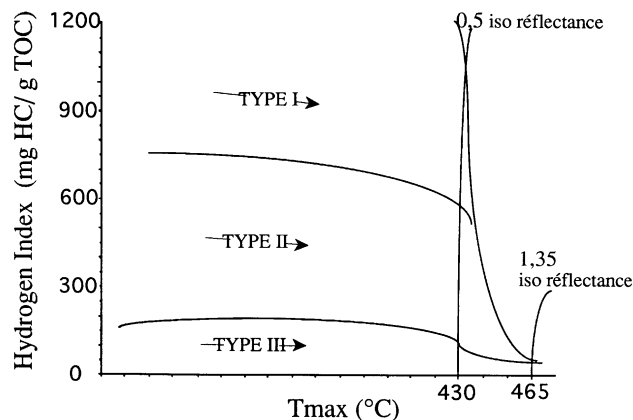


Figure 6. Hydrogen index/Tmax diagram (from Espitalié *et al.*, 1977). Organic type locations

- grey marls (CaCO_3 <50 per cent) sometimes laminated and with some intercalations of sandy layers dated from the Late Glacial to the end of the Preboreal period;
- an alternation of clay, silt and OM-rich carbonate layers (CaCO_3 >80 per cent upstream and >70 per cent downstream) dated from the early Boreal (9000BP) to the end of the Late Atlantic (6000BP) (Di-Giovanni and Campy, 1991);
- a grey-green marly silt, often laminated (CaCO_3 <50 per cent) (Recent Atlantic, Subboreal).

The OM content appears low (<4 per cent) before the Recent Atlantic but increases during and after this age (>4 per cent).

METHODS

Rock-Eval pyrolysis

Rock-Eval pyrolysis (Espitalié *et al.*, 1985a) is a petroleum exploration technique suitable for the study of samples which have previously undergone a thermal diagenetic history. Its application to recent sediments and soils suffers limitations which are detailed hereafter.

The analyses were performed with an Oil Show Analyser (Delsi Instrument). In addition to the classic total organic carbon content (TOC, per cent), the apparatus provides two specific parameters (Espitalié *et al.*, 1985a): the hydrogen index (HI, mg HC/g TOC), and the 'maximum pyrolysis temperature' (Tmax, °C). HI and Tmax determinations are based on the recording of the so-called 'S2 peak' resulting from the emission of hydrocarbonaceous compounds caused by the temperature programmed pyrolysis of the sample under an inert atmosphere (helium). The HI value is equal to the integral of the S2 peak (expressed in mg HC/g rock) divided by the TOC content. Accordingly, the HI value is related to the hydrogen richness of the OM (Crossey *et al.*, 1986) and thus denotes the quality of the OM depending on its maturity and on its biological origin. Three main original OM types can be defined (Figure 6) by analogy with the classic Van Krevelen (1961) classification: lacustrine (I: $\text{HI} > 500 \text{ mg HC/TOC}$); marine (II: $150 < \text{HI} < 500 \text{ mg HC/TOC}$); and terrestrial (III: $\text{HI} < 150 \text{ mg HC/TOC}$) (Espitalié *et al.*, 1977, 1985b, 1986). Note that type II can also correspond to lacustrine OM (Talbot, 1988). Tmax (in °C) is the temperature of the oven at which the maximum generation of hydrocarbons occurs in the course of sample pyrolysis, i.e. at the maximum of the S2 peak. Tmax depends on, and reveals, the level of diagenetic alteration reached by the sample OM, from the beginning of the 'oil zone' ($\text{Tmax} > 430\text{--}435^\circ\text{C}$). Any lower Tmax value suggests only immaturity without more precise significance. In addition, immature samples frequently produce multilobed S2 curves or one peak accompanied with one or more shoulder(s). These various signals correspond to the successive cracking of organic components differing by their own thermal stability (glucides, polypeptides etc. Disnar, 1982; Disnar and Trichet, 1984). In such a case the Tmax value given by the Oil Show Analyser corresponds to the greatest peak.

Unsaturated–saturated hydrocarbon analysis

With the aim of completing pyrolysis results and to obtain information on origins and levels of diagenetic alteration of the sedimentary OM, we also analysed the characteristic unsaturated–saturated hydrocarbon distributions as evidenced by gas chromatography. The dry sediments were twice extracted with acetone/pentane (1:1). The saturated/unsaturated hydrocarbons and the aromatics were separated from the polar organic compounds by column chromatography on Florisil (Merck; 60–100 mesh) by successive elution with n-heptane and n-heptane/toluene (2:1). Gas chromatography (GC) spectra were obtained with a Delsi Instrument D1700 chromatograph equipped with a Chrompack CP Sil 8 CB capillary column (0.22 mm ID; 50 m). After splitless injection at 60°C (1 min), the oven temperature was first increased to 100°C (ramp 30°C min⁻¹) then to 290°C (ramp 3°C min⁻¹) and maintained at the latter temperature until complete elution of all the major peaks.

RESULTS

Soils

In all soils (Figure 7), TOC contents are highest in the upper layers (OL and OF): from 35–40 per cent (peat and soils under *Quercus*, *Quercus–Fagus*) to 10 per cent (meadow) with a mean value in the range 20–25 per cent. TOC contents first decrease with increasing depth but stabilize at 3–5 per cent in the lower layers (A1), except in peat and wet meadow. In the upper layers, HI values are never below 300 mg HC/g TOC except in the soil under *Fagus*. Maximal values are obtained in the peat layers where HI reaches 500 mg HC/g TOC. Except for peat layers, HI values decrease with increasing depth and stabilise at about 100–200 mg HC/g TOC in the lower layers (A1).

The OM of the upper layers (OL and OF) gives low Tmax values (<350°C). The lowest values are observed in meadow environments (<310°C). In contrast, the OM of the lower soil layers (A1) gives rather high Tmax values, i.e. in the 400–430°C range.

Lake sediments

The main Rock-Eval pyrolysis data obtained on the Moulin Bournez core samples are plotted against depth in Figure 8. In order to eliminate perturbations caused by the dilution of terrestrial inputs by authigenic carbonates, the OM contents have been expressed relative to silicates (R ratio). Except for a few discrete levels which are exceptionally rich in OM, R values are rather low along the whole series. However, R values increase rather abruptly from *c.* 0.05 to *c.* 0.2 at the Preboreal–Boreal transition (9000 BP). Similarly, HI values which exceed 175 mg HC/g TOC in only a few levels before this transition, later reach values between 190 and 600 mg HC/g TOC.

Eight samples have been analysed for their hydrocarbon content (unsaturated–saturated hydrocarbon chromatography). The present discussion is limited to unsaturated–saturated hydrocarbon distributions analysed by GC. Three typical gas chromatograms are presented in Figure 9.

In general, the composition of unsaturated–saturated hydrocarbons fractions is characterized by: (i) the small amount or complete absence of low molecular weight compounds (i.e. < about 20 carbon atoms) including isoprenoids such as pristane and phytane, pristene and phytene; (ii) the presence of notable amounts of heavy odd n-alkanes (>n-C₂₀) with a mode in n-C₂₇ or, for one unique sample, in n-C₂₃; (iii) a group of peaks near n-C₂₁ often accompanied by several other products near n-C₂₅. These results are discussed below.

DISCUSSION

Soils

In addition to TOC values, Rock-Eval pyrolysis provides information on the quality of the soil OM, namely HI values. However, the observed variability of HI and Tmax values is such that the soil OM can normally be assimilated to terrestrial type (III) OM, but sometimes also to the marine (II) and even lacustrine (I) OM types defined by analogy with the classic Van Krevelen (1961) classification. This entails that the considered parameters cannot be used to assess of the origin of soil-derived sedimentary OM.

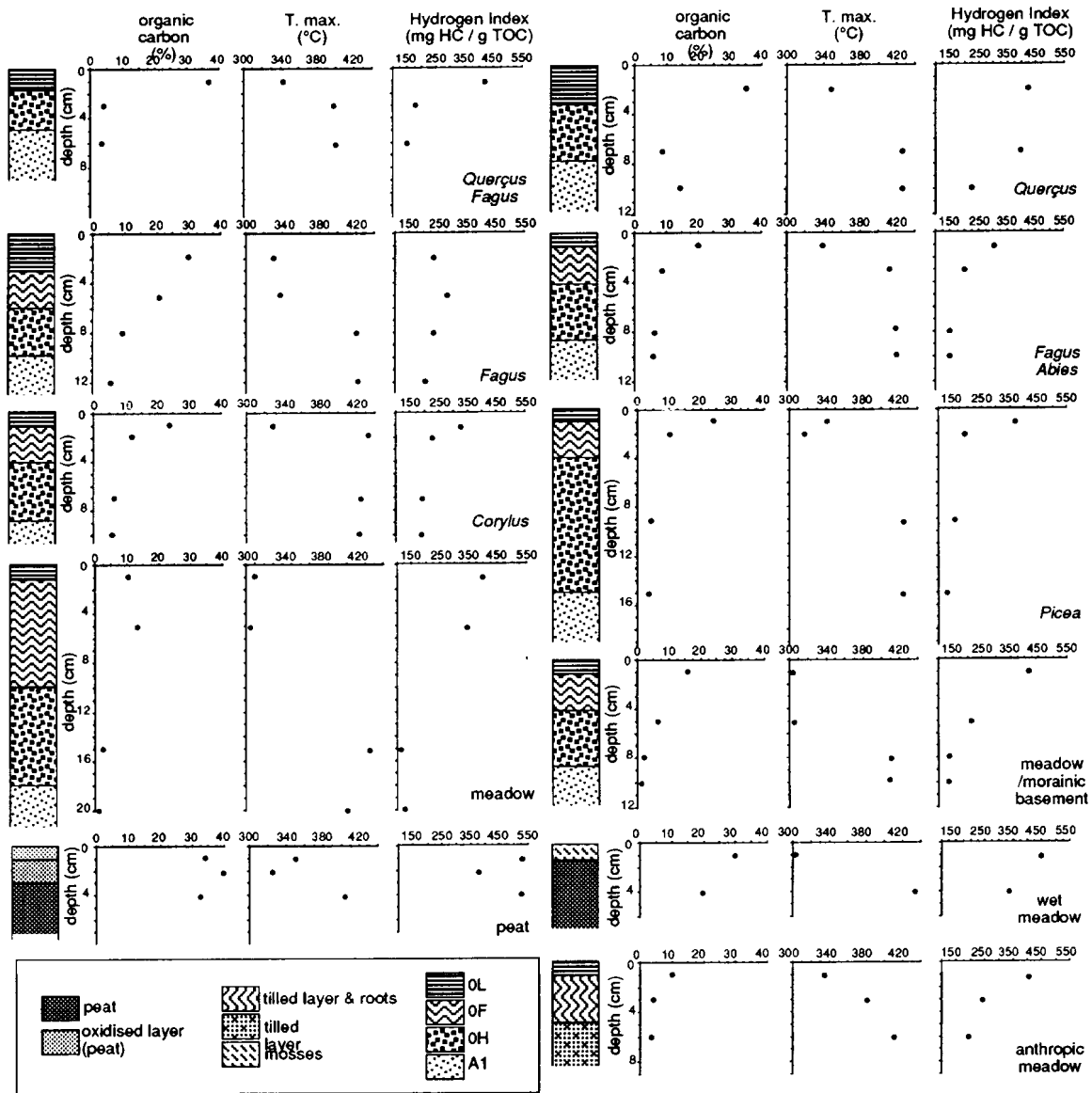


Figure 7. Distribution of organic carbon content, T_{max} and hydrogen index in humus layers plotted against depth

Soil OM maturation increases with depth (Duchaufour, 1977). The upper layers (OL and OF) possess an OM mainly composed of thermally labile biopolymers or at least of poorly altered (or 'humified') OM. Peat and woody fragment samples taken on the watershed produce T_{max} values in the 340–360°C range and HI values higher than 350 mg HC/g TOC (Di-Giovanni, 1994). Thus, in agreement with previous work (Disnar, 1982; Disnar and Trichet, 1984) we can state that such low T_{max} and high HI values indicate thermally labile biopolymers. In contrast, lower soil layers, i.e. the A1 horizons rich in humic substances, produce T_{max} values in the 420–430°C range and HI values lower than 150 mg HC/g TOC. Consequently, such geochemical features appear to be characteristic of humic-like geopolymers (Di-Giovanni, 1994).

With respect to the variability of the organic supply, the studied soils possess identical geochemical characteristics, but do not behave similarly with respect to erosional processes. Indeed, in the case of soils under a forest cover, the litter (OL) is composed of leaves that are easily carried away by runoff. These soils might

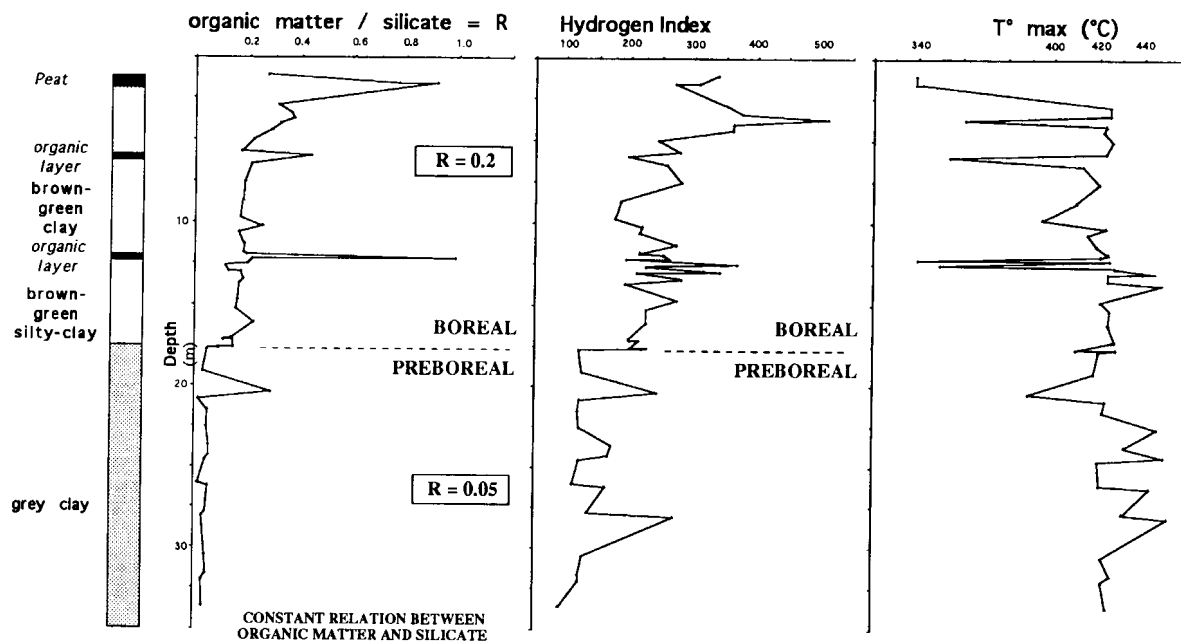


Figure 8. Distribution of the organic matter/silicates ratio (R), the hydrogen index (mg HC/g TOC) (HI) and the maximum temperature (Tmax) versus depth (Moulin Bournez core)

provide an OM coming from the upper soils horizons with low Tmax values (<350°C) and high HI values (up to 300 mg HC/g TOC). In the case of soil in grassland, grasses are not easily carried away by runoff. In that case, the soil particles which are taken away originate mainly from the organo-mineral A1 horizon that contain OM with high Tmax (410–430°C) and low HI values (100–150 mg HC/g TOC).

Lake sediments: origin and preservation of the sedimentary organic matter

Lacustrine organic sedimentation results from competition between the allochthonous inputs carried from rivers and borders of the lake and the autochthonous highly degradable production (Etcheber, 1986; Lin, 1988). An insight into these two sources of OM is provided by the molecular markers present in the hydrocarbon fraction. The lack of isoprenoids (phytane, pristane etc.) derived from the phytol of chlorophyll as opposed to the presence of notable amounts of this pigment revealed by the pronounced green colouration of the organic extracts can be explained by a high preservation of the organic inputs, ensured by rapid burial. n-Alkane distributions dominated by odd C atom numbered n-alkanes in the n-C₂₇ to n-C₃₁ range signify the inheritance from higher terrestrial plants (Tissot and Welte, 1984; Oremland *et al.*, 1988; Vandebroucke, 1980; Wetzel, 1983; Disnar and Harouna, 1994). The marked predominance of this family of compounds in the saturated–unsaturated fractions agrees with pyrolysis data indicating the prevalence of detrital input in the primary sedimentary organic stock. Among the n-alkanes, we see the absence of compounds in the n-C₁₆ to n-C₁₈ range and of distributions dominated by n-C₂₃ to n-C₂₆ without marked odd/even preference. This could indicate either the lack of algal and bacterial inputs, respectively, or that there has been insufficient diagenesis to allow the corresponding n-alkanes to form from their biological precursor compounds – fatty acids or others (Baranger and Disnar, 1987; Baranger *et al.*, 1989; Durand, 1980; Tissot and Welte, 1984). However, GC–mass spectrometry analysis of the compounds forming the two groups of peaks appearing near the n-C₂₁ and n-C₂₅ allows their identification as mono- and di-unsaturated sesqui- and triterpenes, respectively. All these compounds – including diterpenes – are generally referred to as ‘highly branched’ because of their structure: an isoprenic chain bearing an isopentyl or longer radical (Rowland and Robson, 1990, and references therein). The exclusive occurrence of such compounds in lacustrine or marine environments defines them as autochthonous production markers (Rowland and Robson, 1990). GC data show that the proportions of these ‘highly branched

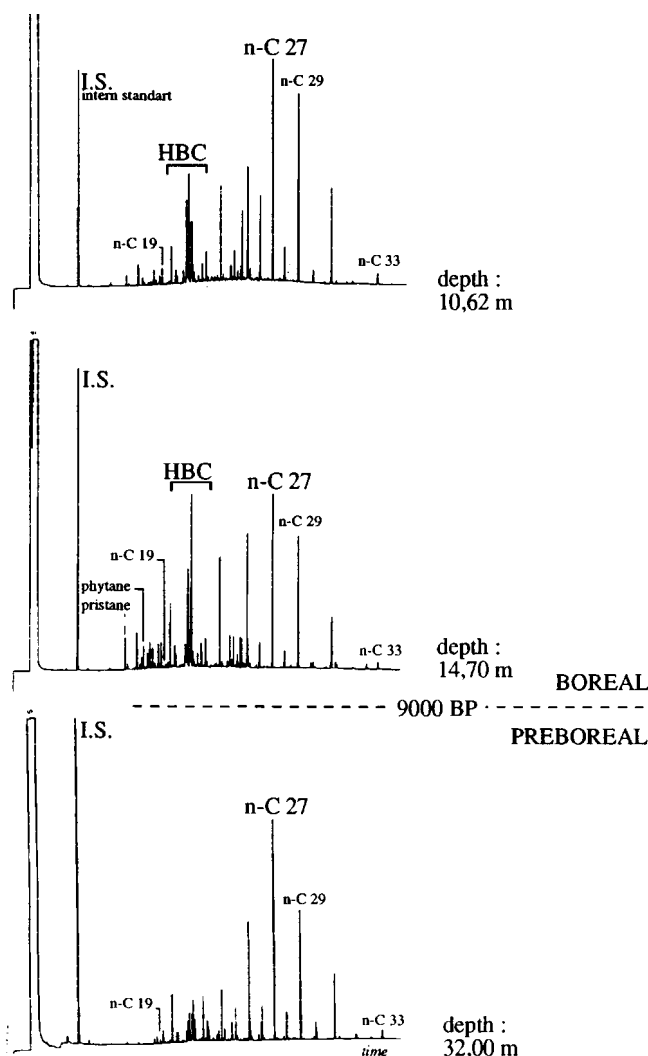


Figure 9. Distribution of the saturated–unsaturated compounds along Moulin Bournez core. HBC = highly branched components

compounds' relative to n-alkanes greatly increase from the Preboreal–Boreal transition (Figure 9), probably due to an increase of lacustrine biological production. However, the following considerations led us to admit that the autochthonous inputs only represented a minor contribution to the sedimentary OM, even after the Preboreal–Boreal transition:

- (i) the lake surface, i.e. the lacustrine production area, covers only 7 km² compared with the 910 km² of the watershed totally covered with forests and rich meadows;
- (ii) the OM/silicate ratio (R), which remains almost constant before and after the Preboreal–Boreal transition, reveals that the sedimentary OM was deposited with silicates (clays) and thus originated mainly from the watershed. The correlation between the silicate content and the TOC (Figure 10) strongly confirms the association of these two constituents.

To summarize the previous discussion, the predominance of odd n-alkanes, the lack of chlorophyll-derived isoprenoids and the low Tmax values are indicative firstly of the immaturity of OM and secondly of its limited alteration during transport and diagenesis. Good OM preservation was probably ensured by rapid burial. Qualitative and even quantitative OM variations, which can be directly considered as representative of the

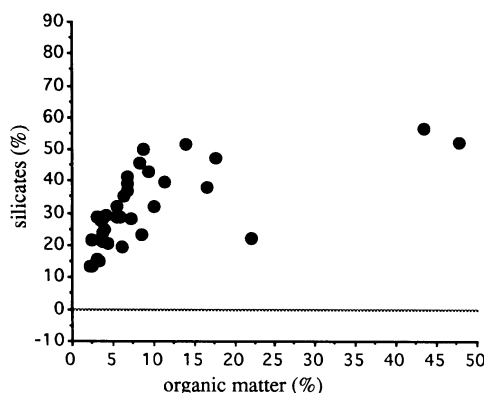


Figure 10. Correlation between organic matter content and silicate content (Moulin Bournez core)

variations of the vegetal cover in the watershed, thus allow a clear separation of the Preboreal and earlier periods from Boreal and younger ones.

The low HI values (e.g. in the 100–120 mg HC/g TOC range) recorded during the Late Glacial to Preboreal times can result either from an oxidation of the primary biological inputs prior to deposition, or from an original organic supply coming from humic-rich soil horizons. Light microscope observations show that the soil-derived sedimentary OM is well preserved, and has not been affected by oxidation during transport and diagenesis (Di-Giovanni, 1994). We thus consider that (i) the organic supply came from humic-rich soil horizons, and (ii) these soils were most probably not protected by a forest cover. OM characterization is in agreement with a minor diversification of the organic producers and the settlement of a vegetal cover on the watershed, following the environmental scarcity of the last pleniglacial period (Würm) (Birks, 1986). Moreover, four Preboreal samples present high Tmax values, in the 440–450°C range. According to the classic Tmax significance (Espitalié *et al.*, 1985a), such values would denote a mature OM, or, more precisely, an OM whose maturity corresponds to the middle of the potential oil window. Such an ancient material could originate from the alteration of the Meso-Cenozoic substratum of the watershed. This observation is consistent with optical recognizance of Meso-Cenozoic organic particles (Di-Giovanni *et al.*, 1997), as well as of calcareous fragments from the bedrock (Campy *et al.*, 1994b). This implies that the soil cover was poorly developed and that the substratum had little or no protection against erosion.

HI values ranging between 200 and 300–350 mg HC/g TOC found after the Preboreal–Boreal transition are typical of well preserved sedimentary OM of terrestrial origin. The HI high OM supply most probably came mainly from soils that have developed under forest cover.

The different TOC and HI levels found on either side of the Preboreal–Boreal transition suggest a significant and surprisingly sudden forest development which announces the climax phase (Duchaufour, 1977) or climatic optimum dated from the Boreal to the Atlantic periods (Campy and Richard, 1987; Richard, 1988; Shackleton *et al.*, 1990).

After the Preboreal–Boreal transition the disappearance of indications of bedrock physical degradation (Campy *et al.*, 1994b; Di-Giovanni, 1994) can result from an increasing and sudden protection of the substratum by the development of soils and forest cover. Einsele (1991), studying several morpho-climatic zones, indicates that chemical denudation rates are smaller than physical ones because of the obvious rule of particulate matter against solute matter in transport phenomena. The transition between physical alteration and chemical dissolution certainly reduced the alteration rate of the bedrock. This obstacle against erosion is a sign of environmental maturation and illustrates that the main morphological characteristics of the Chaillexon basin were acquired before 9000 BP. These results have to be clarified and further morphological investigations have to be carried out, particularly through a comparison between physical and chemical erosion rates.

CONCLUSIONS

The present work allowed the delineation of some gross geochemical characteristics of the soil OM. The

variability of rock-Eval pyrolysis data observed in soils shows that soil OM can normally correspond to terrestrial (type III) OM, but also to marine and lacustrine OM (types II and I, respectively). The upper soil layers (litter) are characterized by high TOC contents, high HI and low Tmax values, while the lower soil layers are marked by low TOC contents, low HI and high Tmax values. Consequently soils under forest cover and soils in open areas can deliver different types of OM, especially because of the presence and nature of the litters (mainly leaves). As a result of this, we suggest that the quantitative and qualitative OM changes observed in the studied sedimentary lacustrine infilling can be interpreted as variations of the original terrestrial organic supply and not as changes in the lacustrine or terrestrial source of the OM.

The Preboreal–Boreal transition (9000 BP) characterizes a major event in the story of the studied limnic system. After this event, the higher plant contribution which becomes notable, is certainly related to forest development. The latter has two important consequences: the development of soils, and the protection of the bedrock from erosion. Among the sedimentary biological markers, a discrete autochthonous signal suggests that this transition also characterizes an increase in the autochthonous production and illustrates an oligotrophic to meso-eutrophic transition due to climatic warming.

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